distillation, exposed to various degrees of temperature below its own boiling point, so long as the hydrocarbons of lighter gravity and boiling point are not removed from the still. Consequently, the liquid hydrocarbons of high boiling point may remain exposed in the still to temperatures below their boiling point for a number of hours. For example, in refinery practice, one to three days is necessary to complete a crude distillation, the exact period depending on the size of the still and the amount of hydrocarbons to be treated. This long exposure to a degree of heat below the boiling point of a particular hydrocarbon, resulting in its dissociation or partial alteration, constitutes "cracking." As time is an important factor in every organic reaction, the technical significance of the time the oil is exposed to heat becomes evident.

It has been pointed out by Engler and Höfer [a] that the separation of hydrocarbons by distillation is often difficult for fractions of petroleum boiling as low as 200° C. on account of the ease of decomposition of the higher-boiling fractions at ordinary atmospheric pressures. Mabery, Zaloziecki, and other investigators have amply established this fact. In some distillation work done by two of the authors [b] it was found that a Pennsylvania oil of the best quality began to crack at 325° C. A similar figure is recorded as beginning the cracking range for Pennsylvania crudes distilled in commercial stills.[c]

FACTORS CONTROLLING CRACKING.

In the cracking of heavy oils two factors govern largely the course of the reactions that take place, namely, temperature and pressure. The function of increased temperature is to break the bonds of groups that make up the complex hydrocarbon molecule. In many processes pressure is of chief importance in controlling the temperature of distillation, but it also exerts an influence on the nature of the decompositions produced.

The temperature at which dissociation takes place with the desired rapidity is usually above the boiling point of the hydrocarbons concerned. When no pressure is employed these hydrocarbons will vaporize and pass out of the reacting sphere, the degree of alteration being small. If, however, sufficient pressure is employed to raise the boiling point to a temperature causing more rapid cracking, alteration into desired products may be obtained with a minimum of total decomposition. As soon as the action begins to be total decomposition, permanent gases will be evolved and both carbon and heavy asphaltic bodies will remain as residues. The volume of gas, therefore, if measured, is an approximate index of the degree of decomposition that is taking place.

[a] Engler, C., and Höfer, Hans, Das Erdöl, vol. 1, 1913, p. 495.

[b] Rittman, W. F., and Dean, E. W., The analytical distillation of petroleum: Jour. Ind. and Eng. Chem., vol. 7, September, 1915, p. 754.

[c] Robinson, F. C., The manufacture of petroleum products: Met. and Chem. Eng., vol. 11, July, 1913, p. 389.

OBJECT OF CRACKING PROCESS.

The cracking process involves, therefore, a partial alteration or dissociation, as distinguished from a more complete alteration or decomposition. The object of cracking is to alter the heavier molecules so that low-boiling hydrocarbons will be produced that would not appear on ordinary distillation. Such a process may or may not be accompanied by an appreciable production of permanent gases, depending on the degree of alteration necessary to obtain the desired products. In a simple cracking process as high a temperature as is practicable within the limits of the apparatus is desirable, in order to insure a high speed of reaction. A decrease in temperature below a given point will mean a decided increase in time. In commercial practice this would mean increase in operating costs. On the other hand, too high a temperature will mean a large production of extreme decomposition products, so that for results desirable commercially a mean temperature must be chosen that will cause the process to be completed at the maximum speed consistent with a relatively small production of permanent gases and carbon. This consideration has been emphasized by Engler and Höfer, [a] who point out that, for the splitting of heavier petroleum hydrocarbons into lighter products, excessively high temperatures are not advantageous.

COMMERCIAL VALUE OF CRACKING PROCESS.

Liquid-phase cracking processes, though extensively used for the production of illuminating oils and motor fuels, are as yet in the primary stages of commercial application. As a means of supplying the products most in demand, their importance can hardly be overestimated. They served their purpose well for producing burning oils, when these were the most desirable products, and are now being adapted to the production of gasolines and naphthas. It only remains to discover the most efficient means of obtaining the maximum possible percentage of the desired product from any particular oil. The ease and cheapness with which crude petroleum can be transported to regions lacking supplies of crude oil give particular value to cracking processes, as the cheapest and most readily obtainable oils may be subjected to cracking at the place of the greatest demand and most extensive use.

[a] Engler, C., and Höfer, Hans, Op. cit., vol. 1, p. 565.